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Polarographic Reduction of Solochrome Fast Navy 2RS in Presence of Bentonite, Kaolinite & Illite Clays

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Aqueous suspensions of the clays bentonite, kaolinite and illite containing solochrome mordant dye have been examined polarographically. The degree of binding of the dye on clay particles at various stages of aggregation has been calculated. The binding of dye on the clay particles involves an anion exchange process which has been supported by the X-ray data of the clay dye-complexes. The expansion of the surface at edges with a simultaneous contraction of the flat unit-layer takes place in the case of bentonite and illite. The data can be possibly used for estimating the anion exchange capacity of the clay minerals.

IN our earlier[1] investigation on the polarographic reduction of methylene blue-clay suspensions we have suggested a more sensitive and accurate method for the identification and estimation of the base exchange capacity of clays. The reduction of azo dyes at the dme has been reported by Conant and Pratt.[2] Recently Malik and Gupta[3] have evaluated the kinetic parameters of the diffusion waves of some solochrome mordant dyes and suggested a mechanism indicating the effect of substituents on their $E_{1/2}$. In the present paper are reported the results of polarographic reduction of solochrome dye (Fast Navy 2RS) in the presence of bentonite, kaolinite and illite.

Materials and Methods

Standard clays bentonite, kaolinite and illite were obtained from Ward's Natural Science Est., New York. The stock clay suspensions were prepared, converted into H-form and estimated as reported earlier[4]. The solochrome dye was purified by recrystallization from 50% EtOH dried over silica gel and tested for purity by chromatography[5]. Britton-Robinson buffers were prepared by the known method[6].

Dye solutions in the concentration range 5×10^{-4}-$1\times10^{-4}M$ were obtained by diluting the stock solutions with doubly distilled water and their *p*H adjusted by adding the requisite amount of the buffer. The dye solution gives a sharp λ_{max} at 510 and 530 nm at *p*H 2·8 and 7·4 respectively. The requisite amounts of the dye ($1\times10^{-4}M$, *p*H 2·8) were taken in eight pyrex glass tubes and 0·0, 50, 100, 150, 200, 250, 300 and 350 mg of bentonite added separately to the different tubes. The total volume in each tube was made up to 20 ml. Polarograms having the same bentonite dye suspensions were also recorded at *p*H 7·4.

Similar sets of dye-kaolinite and dye-illite suspensions were prepared and the polarograms recorded at *p*H 2·8 and 7·4. The amount of dye bound to the three clays, as calculated from the polarograms, are given in Table 1. Polarograms of the dye-clay suspensions at $[dye]=2\cdot5\times10^{-4}M$ and $5\times10^{-4}M$ (when it exists in aggregated form) were also recorded at *p*H 2·8. The binding values of the dye under these conditions are given in Table 2.

TABLE 1 — BINDING VALUES OF THE DYE
$\{[dye]_{initial} = 1\cdot0\times10^{-4}M\}$

Amount of clay (mg)	$[Dye]\times10^{-4}M$ bound to					
	Bentonite at *p*H		Kaolinite at *p*H		Illite at *p*H	
	2·8	7·4	2·8	7·4	2·8	7·4
50	0·20	0·12	0·17	0·08	0·14	0·04
100	0·30	0·19	0·27	0·12	0·20	0·08
150	0·37	0·27	0·34	0·16	0·27	0·12
200	0·44	0·31	0·37	0·19	0·34	0·16
250	0·50	0·35	0·40	0·23	0·37	0·19
300	0·57	0·39	0·47	0·35	0·44	0·23
350	0·67	0·46	0·54	0·39	0·47	0·31

TABLE 2 — BINDING VALUES OF THE DYE AT *p*H 2·8

Amount of clay (mg)	$[Dye]\times10^{-4}M$ bound to		
	Bentonite	Kaolinite	Illite
	$[Dye]_{initial} = 2\cdot5\times10^{-4}M$		
50	0·60	0·45	0·33
100	0·73	0·58	0·48
150	0·93	0·75	0·71
200	1·07	0·85	0·79
250	1·20	1·00	0·94
300	1·33	1·15	1·02
350	1·45	1·25	1·10
	$[Dye]_{initial} = 5\cdot0\times10^{-4}M$		
50	1·70	1·35	1·25
100	2·00	1·50	1·50
150	2·15	1·75	1·75
200	2·55	2·00	1·85
250	2·90	2·20	2·00
300	3·10	2·35	2·13
350	3·35	2·60	2·40

TABLE 3 — X-RAY DATA OF BENTONITE, KAOLINITE AND ILLITE AND THEIR COMPLEXES WITH DYE

Dimensions*	Pure clay		Clay-dye complex at *p*H 2·8	
	2 θ (degree)	d_{hkl} Å	2θ (degree)	d_{hkl} Å
		BENTONITE		
A	6·15	14·37	6·45 (6·29)	13·700 (14·050)
B	35·60	2·522	34·98 (35·40)	2·564 (2.536)
		KAOLINITE		
A	12·45	7·110	12·45 (12·45)	7·110 (7·110)
B	35·10	2·556	34·73 (34·94)	2·583 (2·568)
		ILLITE		
A	8·70	10·16	9·00 (8·80)	9·820 (10·05)
B	35·05	2·560	34·85 (34·90)	2·574 (2·571)

*A = dimentions of basal surface, B = dimentions of edge surface.
The values in parentheses are at *p*H 7·4.

A Cambridge pen recording polarograph was used for recording the polarograms at 30 ± 0·1°C. The capillary characteristics were: $m^{2/3}t^{1/6} = 3{\cdot}75$ $mg^{2/3}$ $sec^{-1/2}$ at $h = 50$ cm and nitrogen was used for the deaeration of solutions. No maxima suppressor was used. The polarographic cell used in these studies was similar to the one used by Beckmann[7] in gas analysis.

The millicoulometric method of DeVries and Kroon[8] was used for determining the value of n, the number of electrons involved in the electrode process.

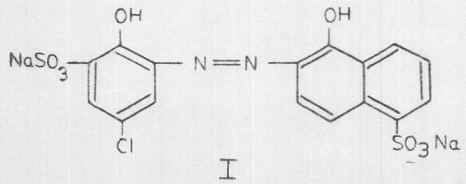
The X-ray diffraction studies of pure clay as well as of clay-dye complexes were carried out on a Philips X-ray diffractometer, the X-ray tube operating at 36 kV and 16 ma with the following diffractometer settings: receiving slit = 0·2 mm, scale factor = 16, 16, time constant = 2, chart speed = 800 mm/hr, X-ray filter = Ni-foil, target material = Cu.

The X-ray data are given in Table 3.

Results and Discussion

The dye (I) exist in a monomeric state at concentrations $<2{\cdot}5\times10^{-4}M$. However, at $2{\cdot}5\times10^{-4}M$ it exists as a dimer and at concentrations $>5\times10^{-4}M$, the dye molecules form a hexamer[3].

The half-wave potentials ($E_{1/2}$) of the pure dye are −0·12 V and −0·48 V at *p*H 2·8 and 7·4 respectively. The limiting currents were found to be diffusion controlled as evident from the linear plots of i versus $h^{1/2}$. Values (1·32-1·63% K^{-1}) of the temperature coefficient also indicated the diffusion controlled nature of these waves. The heights of the waves were found to be *p*H dependent. The waves were found to be totally irreversible when analysed with the help of log plots and also by the criteria of irreversibility as discussed by Meites[9].



I

The reduction of azo compounds at the dme took place at −N=N− giving the hydrazo derivatives. Such a reduction would depend upon the electron density at the double bond which in turn is a function of the substituents in the two moieties. Keeping in view the fact that the reduction of the dye is a two-electron transfer process[8] ($n = 2$) the first step would be the polarization of double bond followed by the protonation of nitrogen at the expense of hydrogen ions from the solutions. A similar mechanism has been proposed by Zuman *et al.*[10] for the reduction of O- and N-substituted oximes.

The addition of even a small amount of clay reduced the diffusion current of the pure dye while the $E_{1/2}$ remained unchanged. However, the most pronounced effect was observed in the case of bentonite. The clays were found to decrease the diffusion current in the order of their anion exchange capacity values which were found to be 7·10, 4·20 and 3·65 meq./100 g of bentonite, kaolinite and illite respectively, as determined by the phosphate adsorption method. This indicated that the uptake of dye takes place primarily through an anion exchange process.

The plots between the decrease in the wave height ($i_{d_0}-i_d$) and the amount of the clays present were linear (Fig. 1). This linear relationship was found to exist even in the case of aggregated state of

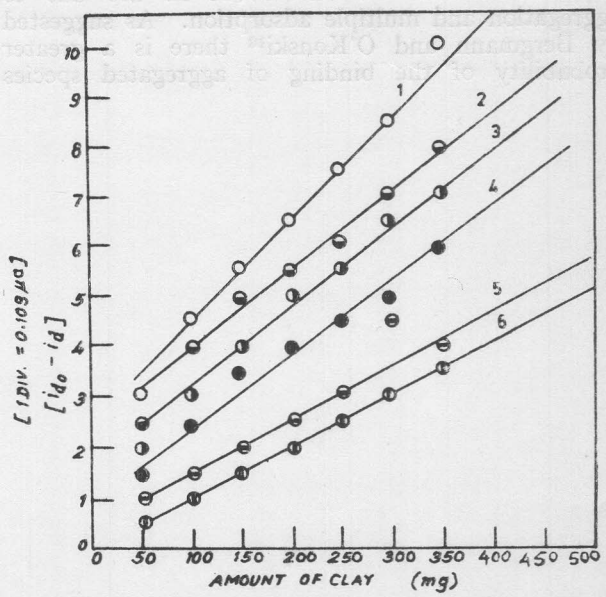


Fig.—Plots of wave height ($i_{d_0}-i_d$) versus amount of clay in the dye-clay complexes. {[Dye] = $1\times10^{-4}M$]; curves 1 and 4, dye + bentonite (*p*H, 2·8 and 7·4 respectively); curves 2 and 5, dye + kaolinite (*p*H, 2·8 and 7·4 respectively); curves 3 and 6, dye + illite (*p*H, 2·8 and 7·4 respectively)}

the dye ($2{\cdot}5\times10^{-4}$-$5{\cdot}0\times10^{-4}M$). Hence, the amounts of free dye from i_d/i_{d_0} values and the amounts of dye bound to the clay minerals were calculated. The amounts of dye bound to the clay minerals at different [dye] and *p*H values are given in Tables 1 and 2.

It was observed that the amount of dye bound in the monomeric state slightly exceeded the anion exchange capacity of each mineral while in the aggregated state the uptake was found to be abnormally large. The binding of anionic dye can be explained in terms of two crystallographically different surfaces on the clay particle each carrying a different type of electrical double layer[11]. The relatively small surface on the edges of the clay particle is positively charged with anions as the counter ions. Since most of the exchangeable anions would be present on edge surface, the uptake of dye should preferentially take place on the edge surface of the clay particle. This is further supported by the X-ray data of the clay-dye complexes which show a distinct increase in the edge surface spacing. The data are: bentonite, 0·042 and 0·014; kaolinite, 0·027 and 0·012; illite, 0·014 and 0·011 Å at *p*H 2·8 and 7·4 respectively. Apart from the expansion observed in the surface at edges, a contraction in the C-axis spacings equal to 0·670 and 0·320 Å for bentonite and 0·340 and 0·110 Å in the case of illite at *p*H 2·8 and 7·4 was also noted. The kaolinite complexes, however, did not show any contraction in the C-axis spacing. The adsorption of anionic organic compounds resulting in an expansion of the edge surface with a simultaneous contraction of the flat unit layer surface in the case of three-layer minerals has not been reported earlier. A possible explanation of this effect needs further investigations and the work in this direction is in progress.

The abnormally large values of the bound dye at concentrations 2·5 and $5\times10^{-4}M$ are due to aggregation and multiple adsorption. As suggested by Bergmann and O'Konski[12] there is a greater probability of the binding of aggregated species as compared to monomeric state on the crystal surface.

The amount of dye bound to the minerals was also found to decrease with increase in *p*H. This is due to the gradual change in polarity of the positive electrical double-layer existing at the edge surface to a negative one with increase in *p*H (ref. 11).

The linearity between the decrease in the diffusion current ($i_{d_0}-i_d$) and the amount of clay added shows that the method can be utilized in estimating the anion exchange values of various clay minerals and in the identification of mixture of minerals having low cation exchange values.

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